HIGH-TEMPERATURE STUDY OF O + H₂CO → OH + HCO

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In our previous studies of the reactions of the methyl radical with molecular oxygen, we noticed that after the methyl radical has been consumed the reactions which control the concentration of hydroxyl are the hydroxyl-hydroxyl self reaction, the title reaction, and the reaction between hydroxyl and formaldehyde. From the long-time temporal behavior of hydroxyl we have been able to extract the rate coefficient for the title reaction over the temperature range 1580 to 2250 K. When we combine our data with the low temperature data of Klemm et al [J. Chem. Phys. 1980, 72, 1256-1264] we obtain the rate expression

$$k(T) = 2.6 \times 10^{-16} \, T^{1.67} \, exp\{-891/T(K)\} \; cm^3 s^{-1}$$

This result is consistent with the earlier recommendation of Herron [J. Phys. Chem. Ref. Data 1988, 17, 967-1026] which is based on a Bond-Energy-Bond-Order calculation adjusted to agree with the experimental results at 700 K.

INTRODUCTION

The reactions of formaldehyde represent an important set of secondary reactions in the combustion of hydrocarbon fuels. Unfortunately, above 1000 K, very few rate coefficients of reactions with formaldehyde have been measured. All of these high-temperature measurements, by different groups or techniques, differ significantly. Previously, only three high-temperature shock-tube studies of the reaction of formaldehyde with atomic oxygen have been published. Izod *et al*[1] estimated a rate coefficient of 1.0×10^{-10} cm³s⁻¹ from 1400 to 2200 K, Bowman[2] deduced $8.3 \times 10^{-11} exp\{-2300/T(K)\}$ cm³s⁻¹ from 1875 to 2240 K, and Dean *et al*[3] concluded the coefficient is $3.0 \times 10^{-11} exp\{-1552/T(K)\}$ cm³s⁻¹ from 1905 to 3045K.

While we were measuring the primary reactions of the methyl radical with molecular oxygen we noticed that as the radical is consumed a formaldehyde molecule and a hydroxyl radical are created. This is independent of the reaction chain which produces formaldehyde. We have taken advantage of this observation to extract the rate coefficient at high temperatures for the reaction of formaldehyde with atomic oxygen from the long-time behavior of our measured profiles of the hydroxyl concentration.

EXPERIMENTAL

The experiments were performed in an ultra-high purity stainless-steel shock tube fitted with two 2"-long windows for optical observations and six pressure transducers for measurements of the shock velocity. The tube has a diameter of 25 mm and the expansion section is 1.5 m long. The methyl precursor, azomethane, was synthesized by the standard method[4] and purified by bulb-to-bulb distillation. High-purity oxygen (99.998%), xenon (99.999%), and helium (99.9999%) were purchased from commercial vendors and used as supplied. Samples were prepared manometrically in a three-liter stainless-steel mixing vessel and introduced into the shock tube from the expansion end of the tube. The purity and composition of each batch of samples were checked by mass spectrometric analysis.

The temporal dependence of the hydroxyl radical was monitored by the tunable-laser flash-absorption technique.[5] The wavelength of the doubled light from a high-resolution (0.02 cm⁻¹ at 618 nm) pulsed dye laser was tuned to the $^{Q}Q_{11}(13/2)$ [$^{\Delta N}\Delta J_{F'P''}(J'')$ notation] transition of the (0,0) band of hydroxyl at 32381 cm⁻¹. An absorption profile at 2200 K is shown in figure 1.

ANALYSIS

In any analysis of a complex chemical system the reduction of experimental data is only as good as the mechanism used to describe the chemistry. A high-speed parallel-processor (Alliant Concentrix 2800) allows us to use a relatively large reaction mechanism for this description. We have constructed a reaction mechanism which contains 25 species and 89 reactions. The mechanism presented by Frenklach *et al.*[6] was used as the starting point. Most of the rate coefficients are from the recent review by Baulch *et al.*[7] The rate coefficients for the major reactions under our experimental situation are given in Table I. At high temperatures the primary reactions which remove the methyl radical and

produce formaldehyde, hydroxyl, and atomic oxygen are

$$H + O2 \leftrightarrow OH + O, \qquad \text{(Rxn. 7)}$$
$$CH3 + O2 \leftrightarrow CH3O + O, \qquad \text{(Rxn. 49)}$$
$$CH3 + O2 \leftrightarrow H2CO + OH, \text{ and} \qquad \text{(Rxn. 51)}$$
$$CH3O (+M) \leftrightarrow H2CO + H (+M). \qquad \text{(Rxn. 76)}$$

Since reaction 76 is relatively fast, for every methyl radical removed a formaldehyde molecule is formed. This is independent of the relative rates of reactions 49 and 51. Also, because reaction 7 is fast a hydroxyl radical is formed for every formaldehyde molecule. Although the concentrations of formaldehyde and hydroxyl are independent of the relative rates of reactions 49 and 51, the concentration of atomic oxygen will depend upon this ratio. Therefore, this approach is only suited for the high-temperature region where the rate of reaction 49 dominates that of reaction 51. The secondary reactions which control the long-time behavior of the hydroxyl radical are

$$OH + OH \leftrightarrow H2O + O, \qquad \text{(Rxn. 11)}$$
$$H2CO + O \leftrightarrow HCO + OH, \text{ and} \qquad \text{(Rxn. 32)}$$
$$H2CO + OH \leftrightarrow HCO + H2O. \qquad \text{(Rxn. 33)}$$

To demonstrate that we can obtain information on the rate of reaction 32 by monitoring the temporal behavior of the hydroxyl radical we used our complete reaction mechanism to perform a sensitivity analysis[8] for hydroxyl at the experimental conditions of the profile shown in figure 1. In figure 2, we plot the square of the reduced sensitivity coefficients with respect to hydroxyl. From this figure we see that immediately after the methyl radical is depleted reaction 32 determines the kinetic behavior of the hydroxyl radical. Reaction 32 produces another hydroxyl radical. Therefore, at long times the profile is controlled by reaction 11. To quantitatively determine the relative importance of each reaction[9] we integrate the squared sensitivity coefficients in figure 2 between 0 and 30 μs. From this calculation we conclude that over the initial 30 μs interval the relative weight of reaction 32 is 26%, for reaction 11 the weight is 53%. The total weight for the sum of all of the reactions which remove methyl is 9.1%. At this high temperature the relative weight for reaction 33 is only 2.7%. A relative weight of 26% is more than sufficient to extract a rate coefficient from an experimental profile. For this analysis we use the recently measured rate coefficient of Wooldridge et al[10] for the hydroxyl-hydroxyl self reaction and vary only the incubation time, the cross section for optical absorption, and the rate coefficient for reaction 32 to fit the experimental profiles. The result of the non-linear least-squares analysis for the profile of figure 1 is shown in figure 3.

As we change the experimental conditions to produce lower temperatures the sensitivity of hydroxyl with respect to the rate coefficient of reaction 32 becomes less important while that of reaction 33 becomes more important. By reformulating the procedure for non-linear least-squares analysis in terms of dimensionless parameters[11] we are able to estimate the relative importance of reactions 32 and 33 for each experimental profile. With this approach we have been able to determine the rate coefficient for reaction 32 from the highest temperature of 2250 K down to 1580 K. Below 1580 K the relative weight of reaction 32 is not large enough to allow us to determine its rate. The results of our non-linear least-squares reduction of the experimental profiles are summarized in Table II.

DISCUSSION

At 2000 K our results are a factor of 1.8 lower than those of Izod et al., a factor of 2.1 higher than Bowman's, and a factor of 3.9 higher than those of Dean et al. All of the above scientists, including ourselves, have numerically integrated the set of differential equation which result from a complex reaction mechanism to deduce the rate coefficient for the O + H₂CO reaction. From our analysis we know that our *best-fit* values for the rate coefficient of reaction 32 are correlated with the value for the rate coefficient for the hydroxyl-hydroxyl self reaction. This correlation may be expressed as

$$\delta k_{32} = 0.672 \delta k_{11}$$

where δk_j is the fractional change in the rate coefficient of the jth reaction. The numerical coefficient was determined by a correlation analysis[9] of the reduced sensitivity coefficients shown in figure 2. It should be obvious that similar correlations may also exist in the previous experiments. These correlations could account for the observed discrepancies. However, before precise statements about correlations can be made it is necessary to carefully compare the mechanisms used for each experiment and perform both a sensitivity and correlation analysis for each set of experimental conditions. Such a detailed discussion is beyond the scope of this preprint.

The rate coefficient for reaction 32 has been measure by Klemm et al[12] between 250 and 750 K. Their results along with ours are shown in figure 4. We have fit both sets of data to the general expression $\ln[k(T)] = \ln A + \beta \ln T - \Delta E/kT$ and obtain

$$\ln[k(T)] = -(35.9 \pm 3.7) + (1.67 \pm 0.47)\ln T - (891 \pm 342)/T(K) \text{ cm}^3\text{s}^{-1}.$$

The confidence limits are at the 95.4% or 2-σ level. These apparently large confidence limits are due to the correlation between the parameters. This correlation may be expressed by the vector

$$S_1 = 0.103\epsilon_{\ln A} + 0.281\epsilon_\beta - 0.382\epsilon_{\Delta E/k}$$

where the ϵ_js represent unit vectors in the 3-dimensional fractional parameter space. The physical interpretation of this vector is that if we change $\ln A$ by 10.3%, β by 28.1%, and $\Delta E/k$ by -38.2% we will move from the minimum value of χ^2 to a point on the $\Delta\chi^2$ surface which defines the 2-σ confidence limits and produces the largest change in all of the parameters. The two curves at the 2-σ confidence limit are shown by the dashed lines in figure 4.

Our analytic expression for the rate coefficient compares favorably with the recommendation of Herron,[13] $5.5 \times 10^{-17}T^{1.94}\exp\{-522/T(K)\}$ which is based upon a Bond-Energy-Bond-Order calculation adjusted to give agreement between experiment and calculation at 700 K. Our expression differs significantly with the recommendation of Baulch et al[7] of $6.85 \times 10^{-13}T^{0.57}\exp\{-1390/T(K)\}$ cm^{3}s^{-1}.

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Table I. Rate Coefficients for some of the reactions of the mechanism.

REACTIONS CONSIDERED	$A(cm^3s^{-1})$	β	$E/k(K)$
7. H+O2<=>OH+O	1.62E-10	0.0	7474
11. OH+OH<=>H2O+O	4.00E-11	0.0	3080
32. CH2O+O<=>HCO+OH	This work		
33. CH2O+OH<=>HCO+H2O	1.25E-11	0.0	84
49. CH3+O2<=>CH3O+O	2.20E-10	0.0	15800
51. CH3+O2<=>CH2O+OH	5.50E-13	0.0	4500
76. CH3O(+M)<=>CH2O+H(+M)	1.00E+15	0.0	17223
Low pressure limit: 0.432E-09 0.0 11065.			

Table II. High-temperature rate data for O + H2CO → OH + HCO.

Mach #	P(kPa)	T(K)	$t_{max}(\mu s)$	N	$rmsd(m^{-1})$	$k(10^{-12}cm^3s^{-1})$	$\sigma(pm^2)$
5.081	186.6	2251	30	271	0.55	66.8	6306
5.072	174.7	2244	60	561	0.51	88.9	5958
4.880	193.2	2100	40	373	0.58	54.3	6087
4.813	188.3	2047	62	547	0.35	69.3	4222
4.689	221.9	1956	68	617	0.61	61.3	4880
4.587	221.1	1891	33	280	0.61	27.4	5450
4.458	221.3	1797	50	438	0.41	46.3	5341
4.321	217.5	1705	58	488	0.44	22.6	5739
4.128	207.8	1580	40	311	0.37	19.0	4749

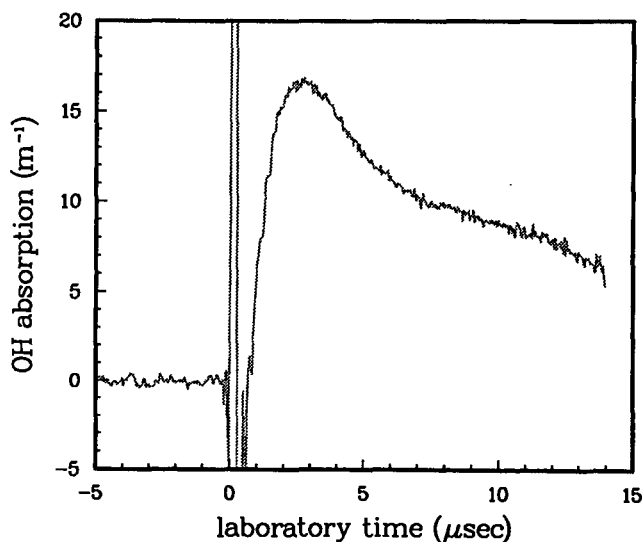For all profiles: $X_{Xe} = 0.49785$, $X_{C2H6N2} = 0.00015$, $X_{He} = 0.198$, $X_{O2} = 0.304$

Figure 1. Absorption profile of hydroxyl at 2244 K and 174.7 k(Pa).
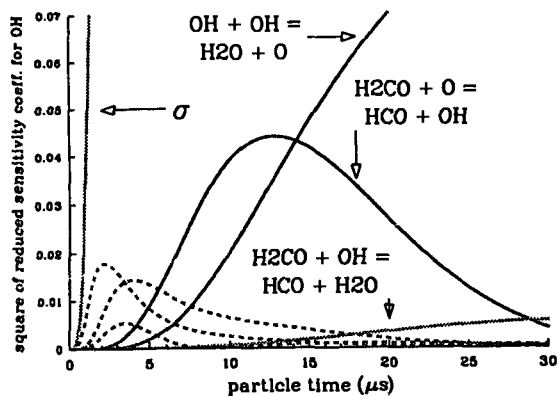The compression ratio, ρ_2/ρ_1, gives $t_{particle} \approx 4.07t_{lab}$.

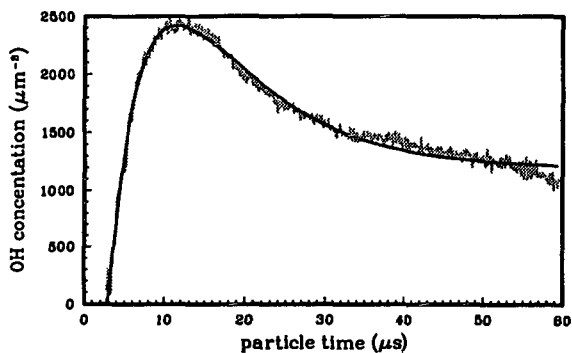Figure 2. Square of the reduced sensitivity coefficients for the profile in figure 1.

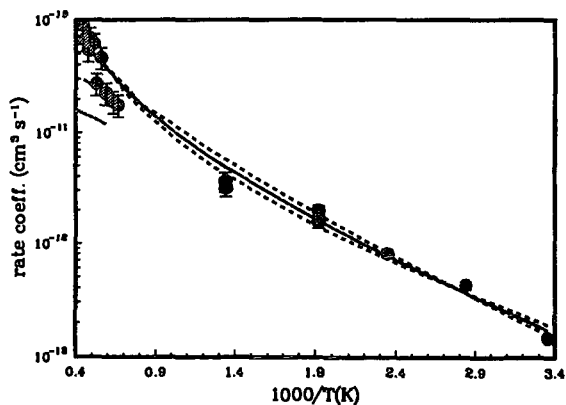Figure 3. Non-linear least-squares fit of the profile in figure 1.

Figure 4. Rate coefficient for the $O + H_2CO \rightarrow OH + HCO$ reaction. The solid line is the best fit to the data and the dashed lines represent the 2-σ boundary.